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(71) Applicant: Minnesota Mining and Manufacturing Company,
Saint Paul, Minn. (US)

(74) Representative: Ruschke, H., Dr.-Eng.; Aguilar, H., Dipl.- Eng.; Patent attorneys
1000 Berling and 8000 Munich

(72) Inventors: Raymond, Albert Ellsworth, Saint Paul, Minn. (US)

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Minnesota Mining and Manufacturing Co., Saint Paul, Minn. 55101, US

Filled polyurethane-latex mass and procedure for the manufacture of a surface coating for leather and leather-substitute materials

The invention concerns the finishing of leather and leather-substitute materials. It concerns in particular the formation of a surface coating over leather materials such as leather layer fragments and deficiently corned upper leather materials, fabrics and materials on leather replacement basis.

In the leather and leather replacement branches of industry, "leather layer fragments" (a thick skin after removing the corned surface) or synthetic substrates are finished and or covered to create a material that looks like corned upper leather skin. However, with all the existing techniques it has proven difficult to find an appealing replacement for corned upper leather skins.

It has been proposed (see Belgian patent disclosure 714 304 of 26 Apr 68) to

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manufacture microporous, water vapor-permeable films from settling but redispersible aqueous polyurethane masses that contain synthetic polymeric fillers, and then to bond these films to substrates. However, this technique, which includes the use of a dispersion that settles, lacks the advantage derived from the use of a non-settling latex. It can also lead to the manufacture of a surface that cannot really be compared to the surfaces obtainable with this invention.

The problems mentioned above are solved by means of the present invention, which proposes a surface coating on irregular leather materials and materials based on leather replacement materials that can be finished using traditional leather-finishing coverings and techniques, yielding a smooth surface of high quality, comparable to that of traditional corned upper leather materials. It is a further goal of the invention to apply the surface coating from a latex system. The invention in addition proposes a compound in which polyurethane-urea latices

are used as bonding agents for the covering mass. Substrates with surface coatings according to the invention also have an excellent appearance and bending strength and could be manufactured with good transmission properties for water vapor.

Summing up, the present invention proposes masses and procedures to cover and to manufacture leather or leather substitute surface coverings onto smooth outer surface irregularities, where the surface covering is receptive to traditional leather finishing agents and can, if necessary, be so finished without substantially changing traditional leather tanning methods. According to the invention, leather and leather replacement materials can be provided with a surface coating to

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create either smooth finishes with the appearance of natural leather, or velvet-like sheet materials with the appearance of suede. The invention uses a thickened polyurethane latex that contains a tough, flexible, organic, small-particle filler such as leather dust, or polymeric particles. The small-particle fillers used in the practical realization of the invention are in the size range of 10 to 150 μm , preferably 15 to 75 μm . In terms of their shape, the filler particles can be shaped as irregular, ground particles, up to more even, spherical shapes as obtained in suspension polymerization. The filler is preferably harder and less elastic than the latex elastomers, thus contributing to the leather-like aspect and feel, in contrast to a plastic or rubber-like feel. The addition of 10 to 60 wt.-% of the filler material (relative to the total solids content of latex) increases not only the breathing capability of the covering, but also creates a surface that surprisingly is receptive to traditional leather finishing agents. The thickened latices used in the practical application of the invention have a viscosity in the range of 30 to 2,500 poise and are best described as having a "mayonnaise-like" consistence. They are applied to the substrates using known procedures, such as applying with blades, rollers, spraying, casting or brushing. The mass can be applied directly to the substrate, or first to a strippable surface and then transferred to the substrate.

For a flat, velvet-like appearance – for instance for women's' shoes – the filler may be in the form of small, brilliantly colored, elastomeric, spherical particles. For darkly colored, finished sheet materials it is preferred to use leather dust as filler, because products can be obtained that look very much like natural leather

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in terms of texture and appearance. Furthermore, films manufactured from the mixture of filler particles such as leather dust and polyurethane-latex, surprisingly have a much higher modulus than films of latex alone. This higher modulus helps to make these films even more leather-like and less rubber-like.

The elastomeric aqueous polyurethane latices than can be used according to the invention in the manufacture of coverings, consist of polyether-polyurethanes, polyester-polyurethanes, polyurethane-ureas, or other urethane latices with the minimum physical properties still to be elucidated here. As the professional knows, polyurethanes can also be manufactured from polyester-ether polyols, or various mixtures of polyesters and polyether polyols with each other and/or with polyamines. For the sake of simplicity, they are all included here under "polyurethane latices". Examples of suitable latices have been proposed in US patent 2,968,575 of 17 Jan 61 (Mallonee) and US patent 3,264,134 of 02 Aug 66 (Vill and Suskind), or in the British patent 1 078 202 of 09 Aug 67. In such aqueous latices the polyurethane chain is lengthened and is present in an emulsified, fine-particle form (i.e., with particle sizes below 10 μm and even below 1 μm). Polyurethanes formed as the reaction product of an organic di-isocyanate with a polyoxy-alkene glycol or polyol, with the chain lengthened with a compound with at least two active hydrogen atoms, for instance water, or a polyamine such as piperazine, dimethyl-piperazine, hydrazine, methylene-bis-3-chloro-4-aniline, 2,4-toluene-diamine, ethylene diamine, polyoxy-alkene-diamines or similar, are preferred. On the other hand, polyoxy-alkene glycols or dimercaptans can be used as chain-lengthening agents. Coverings for leather replacement materials with unusual properties can be manufactured using chain-

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lengthening polymerides obtained by reaction of prepolymers of the polyoxy-alkene glycols with isocyanate end groups and organic di-isocyanates with the diamines mentioned above, or water, to manufacture a polyurethane with a mean molecular weight of at least approximately 10,000, with the physical properties still to be elucidated here.

The polyurethanes that lead to useful leather replacement materials must be elastomeric and creep and flow-resistant at room temperatures. In general they have a brittle temperature of approximately -10°C or lower and preferably, of -30°C or lower. The polyurethanes should exhibit a tensile strength of at least 21 kg/cm^2 and preferably, of at least approximately 70 kg/cm^2 and a fracture strain of at least 300 %, preferably at least 600 %. The modulus (the load at 100 % extension) should lie between 3.5 kg/cm^2 and 70 kg/cm^2 and preferably, between 7 and 35 kg/cm^2 for shoe uppers. These properties can be measured on the polymeride once it is isolated and converted in a suitable manner to a cohesive form, such as a film; the film obtained – for instance a cast film – can be heated or hot-pressed prior to the test, to ensure the effective removal of the solvent, etc. It should be understood, however, that the properties above are only examples of those exhibited by the elastomeric polyurethanes that are useful in the realization of the invention, since the measurements obtained with a given test specimen can vary with the techniques used in the manufacture of the specimen for test purposes. For instance, the properties can be modified by the presence of residual amounts of emulsifier, or by incomplete removal of the

solvent, additional heat-curing that may occur during or after film formation, or by physical processing of the film, or by the presence of humidity. For this reason the values above are only examples of the properties measured on specimens of preferred elastomeric polyurethanes. Test specimens should be manufactured

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using conditions as similar to those obtaining during the manufacture of the coverings according to the invention as is practically possible.

As mentioned above, lengthening the chain of the prepolymer with isocyanate end groups leads to a procedure for the manufacture of polymerides useful to the invention. For instance, prepolymers that carry terminal isocyanate groups can be manufactured by adding one or several polyoxy-alkene polyols, polyoxy-alkene diamines, or polyesters with hydroxyl end groups, to an excess of organic di-isocyanate, performing the reaction in a temperature range between room temperature and approximately 100 °C. Another method consists in allowing the di-isocyanate to react with an excess of polyoxy-alkene glycol, polyester glycol or polyoxy-alkene diamine to manufacture the dimeric glycol or diamine and then saturating this material with isocyanate groups, i.e., adding it to an excess of di-isocyanate to obtain a prepolymer with terminal isocyanate groups. Reactive prepolymers such as these can then be converted to the desired polyurethanes according to the invention by reaction with compounds that have at least two active hydrogen atoms. The expression "active hydrogen" here means hydrogen atoms that show activity in the Zerewitinoff test described in J. Amer. Chem. Soc. **49**, 3181 (1927). Some typical groups are hydroxyl, carboxyl, primary or secondary amino and mercapto groups.

Various organic di-isocyanates can be used for the manufacture of the prepolymer to be used in the invention. Because they are readily available and the fact that they are liquid at room temperature, mixtures of 2,4- and 2,6-toluene-di-isocyanate isomers are preferred. Some other preferred di-isocyanates are 4,4'-diphenylene-methane di-isocyanate and 3,3'-dimethyl-4,4'-diphenyl di-isocyanate. Some other examples of useful aromatic di-isocyanates

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are paraphenylene di-isocyanate, metaphenylene di-isocyanate, 4,4'-diphenyl-di-isocyanate, 1,5-naphthalene-di-isocyanate, 4,4'-diphenyl-ether-di-isocyanate, 3,3'-dimethoxy-4,4'-diphenyl-di-isocyanate, 4-chloro-1,3-phenylene-di-isocyanate, and xylolene. Among suitable aliphatic or cycloaliphatic di-isocyanates are the simple alkene-di-isocyanates such as hexamethylene-di-isocyanate, as well as more complex materials such as bis-(2-isocyanato-ethyl)-carbonate, bis-(2-isocyanato-ethyl)-4-cyclohexene-1,2-dicarboxylate, bis-(2-isocyanato-ethyl)-1,4,5,6,7,7'-hexachloro-5-norbornene-2,3-dicarboxylate.

The polyoxy-alkene glycols used in the manufacture of such prepolymers or polyols have molecular weights that generally lie in the range of approximately 300 to 5,000 and preferably, approximately 400 to 3,000; the more elastic polymerides are normally obtained from higher-molecular glycols. Some examples of such polyoxy-alkene glycols are polyoxy-ethylene glycol, polyoxy-propylene glycol, polyoxy-tetramethylene glycol and higher polyoxy-alkene glycols. These polyether glycols are manufactured using the generally known ring-opening or condensation polymerization. If these polyols contain recurring oxyethylene groups, the total weight fraction of such oxyethylene groups should be controlled, since this structure tends to confer water sensitivity to the finished product. Other suitable polyols are castor oil, polybutadiene with terminal hydroxyl groups and vinyl polymerides with terminal hydroxyl groups, preferably in the molecular weight range of 500-5,000.

Polyoxy-alkene diamines manufactured from polyglycols such as polyoxy-propylene glycol can also be used to manufacture useful polyurea materials or polyurethane-ureas as described in US patent 3,179,606. Such diamines usually have molecular weights of approximately 500 to 10,000.

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Polyester glycols or polyols can be used by themselves or together with polyether glycols or polyols in the manufacture of the prepolymers used in accordance with the invention. Polyester glycols or polyols can for instance be manufactured by reaction of dicarboxylic acids, esters or acid halides with simple glycols or polyols. Among suitable glycols are ethylene-, propylene-, diethylene-, dipropylene-, tetramethylene-, and decamethylene glycols, 2,2-dimethyl-1,3-propanediol and cyclic glycols such as cyclo-hexanediol. Polyols such as glycerin, pentaerythritol, trimethylol-propane and trimethylol-ethane can be used in limited amounts to introduce chain-branched points in the polyesters. These hydroxy compounds are reacted with aliphatic, cycloaliphatic or aromatic dicarboxylic acids or low alkyl esters or ester-forming derivatives of them, to manufacture polymerides with terminal hydroxyl groups. Characterized by molecular weights of approximately the same order of magnitude as those mentioned for the polyoxy-alkene glycols above, preferably their molecular weights lie between 400 and 4,000 and in particular, at approximately 1,000 to 2,000. Some examples of suitable acids are for instance succinic, adipic, suberic, sebacic, phthalic, isophthalic, terephthalic and hexahydro-terephthalic acids and the alkyl and halide-substituted derivatives of these acids.

A prepolymer can be obtained in the presence or absence of a solvent, although the presence of a solvent often facilitates mixing and handling. It is possible to use ordinary solvents inert towards isocyanates, such as toluene, xylenes, etc. Chain lengthening of the prepolymers can be accomplished partly in solution, prior to emulsification. In this context, small difunctional molecules such as

diethylene glycol or diamines can be used as chain-lengthening agents, to increase the density of polar sites on the finished prepolymer, and thereby to

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improve such physical properties as the modulus and the tensile strength. In a similar manner, the prepolymer can be partially reacted with other glycols, or other difunctional or trifunctional materials in such amounts that the finished reaction product still retains isocyanate end groups.

The prepolymer is finally emulsified in water and diluted with water or polyamine during the emulsification procedure, as described in the methods of Mallonee in US patent 2,968,575, or by Wyandotte in British patent 880,665, or by Vill and Suskind in US patent 3,264,134. The professionals can find other suitable latices.

In some cases the filler particles can be prepared directly during the emulsion polymerization step, by performing the emulsification step with reduced stirring. It is possible in this manner to prepare a mixture of small latex particles and larger (bigger than 10 μm) spherical particles in one operational step. On the other hand, two separate latices can be manufactured, one with larger, preferably harder particles and the other one with smaller, preferably more rubber-like particles.

The prepolymers can be similarly modified before chain-lengthening, with other constituents such as softeners, dyes, pigments, smaller amounts of other compatible polymerides, or with agents that contribute to light, heat or oxidative resistance, as long as the elastomeric character of the polyurethane is not lost.

Phosgene chemistry could be used directly in the manufacture of prepolymers, as an alternative to the use of a di- or poly-isocyanate. As is generally known, it

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is possible for instance to react phosgene with a diamine to obtain a prepolymer with a terminal isocyanate group. In a similar manner, carbonate esters can be reacted with diamines to manufacture prepolymers with terminal isocyanate groups.

In order to obtain microporous polymeric films or coverings with the greatest stability of the microporous structure at room temperatures, it is desirable for the polymeric material to be crosslinked, as this reduces its thermoplasticity. Such crosslinked products also have better bending strength and are more resistant to solvents and have many other advantages. The extent of crosslinking required depends on the mean chain length of the polymeric material obtained. Crosslinking should not be sufficient to depress the last fracture strain to less than 300 %. Polyurethanes with a crosslinking density of approximately one

cross-linkage per 5,000 to 15,000 atomic weight units of the polymeride are preferred. Less crosslinking is necessary in the case of very high-molecular polymerides. Chain branching of the polymeride can also be accomplished by heating the prepolymer or the finished polymer to high temperatures.

The polyurethane latices that can be used for these coverings can be anionic, cationic or non-ionic, but it was found that for most purposes, anionic latices are the easiest to process and the most useful.

During the manufacture of these coverings on a porous substrate, it is preferred to add a thickener to the latex, so that the end viscosity of the covering material falls within the range of 5,000 cps and preferably, more than 10,000 cps. Such thickened materials are easily applied to permeable substrates and form even coatings.

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Among the suitable thickeners are finely comminuted silicic acid, polyacrylic acid thickeners, methyl-cellulose, carboxymethyl-cellulose, polyvinyl pyrrolidone and such.

If the thickened latices are applied in accordance with the invention onto an open, porous surface - such as a fabric - in a single thick coat in such a way that all surface irregularities are covered, the film obtained is smooth and free of many of the deficiencies that normally appear when a number of thin coats are applied to the same support. In addition, using a thickened latex, the extent to which the support is impregnated, or the substrate is penetrated is reduced to an insignificant amount. Furthermore, in systems that are pigmented or that contain fillers, where the material added is of large particle size and normally would tend to sediment, using the thickened latex keeps the particles in homogeneous suspension, such that a homogeneous coating with good appearance is obtained, in contrast to the coverings that could be obtained using coatings with a latex of lower viscosity.

Leather dust, for instance obtained by collecting milled tanned leather from the grain side of chromium-tanned skins, can be classified into a satisfactory size by removing any material that does not pass through a 40 mesh screen (Tyler, US or British standard). (In any event the mean diameter of the particles that pass through the 40 mesh-screen should be within the range specified by this invention). The use of approximately 10-40 % leather dust relative to total weight of the dried coating yields good results, with the use of 25 wt.-% preferred. If they are not completely smooth, such coverings can be easily polished to a quality that strongly resembles that of quality upper leather.

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When they are applied to split hide leather, the product has an unusual appearance, hand and rupture and can additionally be finished with traditional leather finishing products.

It is also possible to admix colored polyurethane or other rubber-like spherical particles, usually in amounts of 25-60 % of the total weight of solids, to the thickened polyurethane latex. Coverings of such mixtures have a fine suede-like, non-glossy, pleasing appearance. If a mixture of colors is used to obtain a combined color, such as red, yellow and blue to obtain brown, then an especially appealing appearance is obtained.

As mentioned earlier, colored polyurethane beads can be manufactured simultaneously with the manufacture of the latex, using a pigmented prepolymer and gentle stirring during the emulsification process.

Many resins that can be used in the manufacture of these products as fillers, are available in the right particle size range. Colored particles can also be obtained by milling colored resins, for instance polyvinyl chloride, to the right size, or by precipitation from a solution. Some polyvinyl chloride can be used together with other particles, imparting wear resistance to the covering obtained.

A preferred implementation form of this invention consists in the use of a solvent-free organic liquid, not miscible with water, high-boiling, finely dispersed in the thickened latex coating mass that imparts the desired high permeability for water vapor to the coating obtained. Such liquids usually have a boiling point of approximately 150-300 °C, such that upon frying the water is evaporated first from the latex and then the organic liquid can be evaporated, such that after the

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evaporation microporous channels remain in the covering, permitting the passage of water vapor.

The organic liquid should not be a solvent for polyurethane or the small-particle filler. Among suitable organic liquids for this application are the mineral spirits with a boiling point above 65.5 °C, hexadecene, dodecene and dodecyl chloride.

On the other hand, microporosity can be achieved by freeze-coagulation of the polymeride, or other known techniques, for instance the generally known brine technique, or the technique disclosed by Raymond et al. in US patent 3,436,303 of 01 Apr 69, or the corresponding French patent 1 501 816 of 09 Oct 67.

The microporous polymeric materials applied to such substrates usually have a thickness after drying of 75 to 750 µm and preferably, of approximately 125 to 375 µm. The coatings can be applied onto suitable substrates by blade-coating, spray coating, roller-coating, brushing, extruding, or any other suitable technique.

It is possible to form unsupported films by the procedure according to the invention and the latex polymeride can be reinforced by the addition of fibers to improve tear resistance and tensile strength. In this case the films are usually cast on a glass or stainless steel support that allows an easy removal of the film after drying. If necessary, such films can be layered on a suitable substrate.

It is often desired to add a fibrous material to the latex polymerides used in the procedure according to the invention, to reinforce the polymer after application.

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Such fibrous materials are usually used in small amounts that are sufficient to provide the required reinforcement. Larger amounts can be used if the fibers are so fine that they don't affect the feel or the texture of the finished covering excessively.

Example 1

Chromium-tanned leather polishing dust (Trostel Tanning Co.) was sent through a wire mesh screen with 0.4 mm openings, with mechanical shaking. 180 g of the leather dust from this screened batch were added to 450 g mineral spirit and manually mixed until the entire leather dust was absorbed by the mineral spirit (boiling point 160-200 °C). 60 g oleic acid USP were then added to that mixture and stirred in manually. 60 g of 28 wt.-% ammonium hydroxide were added to the mixture and mixed manually for several minutes. The oleic acid and ammonia react to form ammonium oleate, a surfactant that contributes to wetting the leather with the mineral spirit and dispersing it in the latex. The paste-like mixture obtained was then allowed to stand for several minutes. 450 g tap water were then added to the mixture and stirred with an air motor, at a relatively low speed. 1040 g of an anionic polyurethane latex with 51.4 wt.-% total solids content (Wyandotte Chemicals Corp. X-1028 latex) were added to the mixture while the mixture was continuously stirred with the air motor. Another 500 g tap water were then added to further reduce the viscosity. 9 g of a dry sodium salt of a condensed naphthalene-sulfonic acid (Rohm and Haas Company Tamol N) were added to the finished mixture and allowed to mix for approximately 15 minutes. The mixture was then stirred in an Eppenbach Homo-Mixer for 15 min, at fairly high speed (Variac setting – 70). The mixture was allowed to cool to ambient

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temperature (22 °C) and then sprayed with an airless spray pipe with a tip opening of 0.38 mm, at an air pressure of 4 atm, onto a chromium-tanned split hide leather that had been coated with a thin layer of an emulsified reaction product or organic di-isocyanate and polyalkene-ether glycol, chain-lengthened

with water, to a thickness of 1.14 mm. The viscosity of the coating mixture was of 18,600 centipoise at 21 °C. The sample was then placed in an air-operated oven at 49 °C for 16 h. Then the sample was polished to smoothness with 400 grit sandpaper; the end covering thickness was of approximately 0.38 mm.

Then a commercially available aqueous finishing system of acrylic type was sprayed onto the sample in three coats. The sample had a smooth, leather-like appearance. The water vapor permeability found for the coated specimen was of 420 g water transported water per 100 m² per h. A 40 mm x 70 mm rectangle was cut out of the specimen and placed on a bending machine (Bally). The coated specimen could be bent 70,000 times before failing. The same figure was obtained for the uncoated split hide leather.

Example II

Example I was repeated, except that the condensed naphthalene-sulfonic acid was omitted. The mixture had a viscosity of 27,000 centipoise and could be readily sprayed; however, several deficiencies were observed in the coating.

The WVT of the coated split hide leather was 550 g, the bending time to failure was 700,000.

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Example III

The following materials were manually mixed in a half-liter beaker:

30 g chrome-tanned leather dust, sent through a screen with 0.4 mm openings (Tyler mesh 40); most particles were of a size between 10 and 50 µm.
75 g mineral spirit (boiling point 160-200 °C)
10 g oleic acid
70 g 10 % aqueous sodium hydroxide, and
21 g tap water.

Once the mixture was homogeneous, 209 g Wyandotte E-411 polyurethane latex (90 g solids) were added.

The mixture was then stirred for 30 seconds with a sharp shearing mixer. It was viscous enough for the surface to remain deformed when it was stirred.

After centrifuging to remove air bubbles, the mixture was applied with a blade to a cotton fabric at a wet thickness of 1 mm. The coating was dried for 16 h at 65 °C and heated for 30 min at 150 °C.

The coated fabric had a water vapor permeability (WVT) of 16.4 g per m² per h and could be bent 1.28 million times on a Newark leather-bending instrument (commercially available from the Newark Leather Finishing Co.); the test was terminated at this point, even though no deficiencies were observed. A similar coating, prepared with ammonium hydroxide instead of sodium hydroxide, was viscous but separated after stirring. A coated fabric had a WVT of 9.7 g/m² per h. It could similarly be bent 1.28 million times without failing.

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The water vapor permeability was measured by covering a cup containing water with the test specimen and then measuring the weight loss at an outer atmosphere of 50 % relative humidity and 21 °C over a 24-48 h period of time.

Example IV

A polyether-polyurethane latex with 42.3 % solids was obtained by emulsifying a prepolymer in water that had been manufactured by reacting 21.0 mol polyoxy-propylene diol with a mean molecular weight of 2,000 and 5.4 mol polyoxy-propylene triol with a mean molecular weight of 425, with 58.5 mol toluene-di-isocyanate (TDI) (2,4:2,6-isomers in a 80:20 ratio) at 85 °C, for 3 hours, until an isocyanate equivalent of 928 was obtained. This mass had a composition of 1 triol unit per 10,000 hypothetical atomic weight units. A dried film heated for 20 min to 150 °C and then kept cooled to 21 °C at 50 % relative humidity had the following physical properties, measured on an Instron Tensile Tester using a 0.317 mm wide dumbbell specimen and a jaw distance speed of 50.8 cm/min

Tensile strength	69 kg/cm ²
100 % modulus	8.4 kg/cm ²
% elongation at rupture:	970 %

Covering dispersions were manufactured using this latex and two filler mixtures of chrome-tanned leather dust as in Example III, with Tyler mesh 40. Part of the tanned leather dust was mixed with 2 ½ parts mineral spirit (boiling point 160-200 °C) and ½ part each of oleic acid and concentrated aqueous ammonia. The mixture was added to the latex mentioned above and yielded mixtures containing

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10 wt.-% and 25 wt.-% leather dust, relative to solids. The mixture was stirred briefly with a high speed mixer and centrifuged to remove air.

The viscosities, measured with a Brookfield Model RVF Helipath Viscosimeter at 25 °C, were:

For the 10 wt.-% leather dust specimen	285 poise
For the 25 wt.-% leather dust specimen	4750 poise

Blade coatings (0.1. mm distance) were prepared with each sample, on untreated cotton fabric and on polyester film. The coatings on fabric were dried on an air-operated oven at 65 °C. The coated polyester films were air-dried. Both were melted at 150 °C for 30 minutes and subsequently reconditioned at 21 °C and 50 % relative humidity. The coverings prepared on polyester films were peeled off and tested for tensile strength, modulus and elongation. The covered fabric specimens were checked for bending resistance and water vapor permeability.

The following results were obtained:

Leather dust, wt.-%	Tensile strength in kg/cm ²	100 % modulus, in kg/cm ²	Elongation %
10	24	17.6	510
25	18.3	18.3	100

Leather dust, wt.-%	WVT g/m ² /h	Bending strength (Newark)
10	24	no failure to 4,000,000
25	18.3	no failure to 4,000,000

The two coverings were able to incorporate aqueous standard leather finishing agents and the finished coverings were of similar appearance. The coverings

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with 25 wt.-% leather dust were more leather-like in their feel than those with 10 wt.-%.

Example V

A covering dispersion was manufactured as in Example IV, from the following formulation:

30 g chrome-tanned leather dust, 40 mesh (Tyler)
 75 g mineral spirit
 15 g oleic acid
 15 g concentrated ammonia (28-30 % NH₃)
 38 g water
 212 g latex, as described in Example IV, with 42.4 % solids

The viscosity of the mixture was 455 poise. The mixture was applied with a blade (0.1 mm distance) on a needle-stamped, non-woven polypropylene ribbon that had been coated and filled with a polyurethane latex (Wyandotte E-207) and had a thickness of approximately 0.15 cm.

The covering was then dried for several hours at 65 °C and then subjected to a melting cycle at 150 °C for 45 min and then reconditioned at 21 °C and 50 % relative humidity.

The covered non-woven ribbon was bent on a Bally bending test facility and failed after 147,000 passes.

This structure can be finished with the traditional leather finishing agents and has the appropriate strength, wear resistance and bending strength to be used in upholstery or for shoe uppers. It has excellent layer fractioning characteristics, similar to those of high quality leather.

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Example VI

Four cationic latices were manufactured using the operating procedure of Suskind in French patent 1 410 546, disclosed on 02 Aug 65. The polymerides are chosen such that on the average they have 1 mol of triol per 15,000, 10,000 and 7,500 hypothetical mean atomic weight units and were correspondingly identified with the numbers 1, 2, 3 and 4; they were prepared using the following formulations:

No. 1 A) 300 g diol of mean molecular weight 1968
B) 10.66 g triol of mean molecular weight 424
C) 66.3 g TDI (80/20 2,4-/2,6-isomers)
D) 7.54 g methyl-diethanolamine (MDEOA)

No. 2 A) 300 g diol
B) 16.66 g triol
C) 73.6 TDI
D) 7.80 g MDEOA

No. 3 A) 300 g diol
B) 22.9 g triol
C) 81.9 g TDI
D) 8.08 g MDEOA

No. 4 A) 300 g diol
B) 37.0 g triol
C) 98.6 g TDI

D) 8.71 g MDEOA

The amounts A, B and D were weighed into bottles and mixed to homogeneity. The amount C was admixed, the bottles were closed, placed in a roller mixer and left exothermally for 2 hours and then placed in an oven at 65 °C for 2.5 h and then returned to the roller for 40 h at room temperature. Each of these mixtures

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was then emulsified in water that contained acetic acid and this with the aid of a high-speed mixer and then was allowed to stand for several days, prior to being used. The emulsion formulations and the % of solids of the latices are listed in the Table below:

No.	Prepolymer parts	Water parts	Acetic acid parts	Solids, wt.-%
1	384.5	557	11.6	34.2
2	398.06	600	12.0	36.7
3	411.88	618	12.4	42.3
4	444.31	668	13.4	36.3

Covering dispersions were prepared with each of these four latices, by mixing 30 g of 40 mesh chrome-tanned leather dust with 75 g mineral spirit (boiling point 160-200 °C), 15 g water and sufficient latex to obtain 90 g polymeride solids. Enough water is added above to obtain a total weight of 425 g. The constituents are mixed in a strong shearing mixer, then centrifuged to remove any enclosed air bubbles.

A 0.1 mm (wet) blade coating of each dispersion was applied to an untreated cotton fabric, dried for 3 h at 65 °C, melted at 150 °C for 30 minutes and then reconditioned at 21 °C and 50 % relative humidity.

No.	Hypothetical cross-linking density	WVT g/m ² /h	Viscosity poise	Newark bending (passes to failure)
1	1/15,000	5	5,500	5,300
2	1/10,000	5.3	1,900	668,000
3	1/7,500	4.6	250	668,000
4	1/5,000	4	2,900	5,300

With this system, a hypothetical crosslinking of 1 triol per 7,500-10,000 atomic mass units of polymeride is preferred, as it yields maximum bending strength.

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Example VII

400 g of polyether-polyurethane prepolymer from Example IV (with 75 % solids, 25 % toluene) were emulsified for 3 min in 500 g water using a high-speed mixer. 3.71 g of 64 % hydrazine were added and emulsification continued for 15 sec. The latex was allowed to stand for several days and then toluene was removed azeotropically under a vacuum. The latex had a solids content of 42.4 %.

A film manufactured with this latex had the following properties:

Tensile strength	78 kg/cm ²
Modulus (strain at 100 % elongation)	11.3 kg/cm ²
% elongation at rupture	660 %

A covering dispersion was manufactured with the above latex and 25 % 40 mesh chrome-tanned leather dust, as in Example III. The viscosity was 430 poise.

A covering prepared on fabric as before had a WVT of 4 g/m²/h and could be bent 2.5 million times on a Newark bending apparatus without failing. This covering compound is similar to that of Example II, except that a diamine was used for chain lengthening. A higher modulus led to a somewhat improved wear resistance.

Example VIII

A series of latices was manufactured as in Example IV, but using different triol

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amounts. Covering compounds as manufactured in Example IV were applied to a fabric and after drying and heating, were tested for bending strength.

	Hypothetical atomic weight units per mol triol	Newark bending cycles to failure
a	50,000	1,000 passes
b	32,000	1,000
c	18,000	18,000
d	13,000	650,000
e	10,000	>1,800,000
f	8,000	> 1,300,000
g	6,000	> 2,000,000
h	4,000	800,000

The coated fabric of specimen d was in addition heated for 1 h to 150 °C and then required 1,270,000 bending passes to failure. The coated fabric of specimen

h was additionally heated for 1 h at 150 °C and then resisted 2,000,000 bending passes without failure.

Example IX

A polyester-polyurethane latex was prepared by emulsifying 1,500 g of an isocyanate group-carrying polyester with hydroxyl end groups (Witco P611), diluted with toluene to 75 % solids, in 2,260 g water. Toluene was azeotropically distilled off under a vacuum. The latex obtained had 53.3 % solids. A covering dispersion was manufactured with this latex, using the following formulation:

30 g chrome-tanned leather dust (40 mesh screen)
 75 g mineral spirit
 15 g oleic acid
 15 g concentrated NH₃
 169 g latex with 53.3 % solids
 50 g water

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The viscosity after mixing was 375 poise. A 0.1 mm blade coating (wet) was manufactured on an untreated cotton fabric, dried at 65 °C, sent through a melting cycle at 150 °C for 30 min and at 200 °C for 10 min, then reconditioned at 21 °C and 50 % relative humidity. It had a WVT of 4 g/m²/h. This covering could be finished with traditional leather finishing agents and had excellent wear and abrasion resistance. It was hence especially useful wherever rough handling can be expected, as with luggage.

Example X

A latex was manufactured as in Example IV, except that the prepolymer was diluted with toluene shortly before emulsification, certain pigments were added and the mixture was sent through a stone mill to obtain an appropriate dispersion. The latices obtained had large and small particles. The largest particles were beads with a diameter of approximately 80 µm that served as small-particle fillers.

Latex	Pigment		Vendor	g prepolymer (75 % solids)	% pigment	g H ₂ O	WVT for coating obtained
	Color	No.					
1	Red	9273	Drakenfeld	1,600	90	2200	
2	White	RA	Titanox	1,600	90	2200	
3	Blue	F18029	Ferro	1,600	90	2200	
4	Yellow	1079	Reichhold	1,600	90	2200	10.6
5	Black	10R	Cabot	1,600	30	2200	5.5
6	Polished	F17126	Ferro	1,600	90	2200	8
7	green						

	(mixture of above latices) 7.3 % red 10.4 % white 41.8 % blue 32.2 % yellow 8.3 % black	8.3
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Toluene was removed from the latices obtained by azeotropic distillation under a vacuum. They were then thickened with a polyacrylic acid thickener and the acidity was adjusted to pH 6.5-7.0 to achieve the thickening. The mixtures had viscosities of approximately 200 poise. The surface of the mixture remained deformed when it was stirred.

A 1 mm blade coating on fabric was prepared with each of the thickened latices and dried at 65 °C for 1 h and the for 45 min at 150 °C.

Because of the crosslinked spherical particles present, the surface of the coverings did not sparkle. Mixtures of pigmented latices were also prepared. These surfaces were similarly non-sparkling and had an appearance similar to suede because of the identifiable particles of the different colors. These coatings are especially desired in women and children shoes, in upholstery and wear articles, where the suede-like appearance and brilliant colors contribute to the style.

Example XI

Covering dispersions were manufactured using the latex from Example IV and blue-pigmented, crosslinked polyester-polyurethane beads with a particles size of 10 to 75 µm, mostly 20-25 µm.

The following formulations were used:

10 % beads 12 g blue urethane beads
250 g latex with 43.2 % solids
50 g 2 % polyacrylic acid thickener
1 g aqueous ammonia

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25 % beads 30 g blue urethane beads
208 g latex with 43.2 % solids
70 g 2 % polyacrylic acid thickener
1 g aqueous ammonia

50 % beads 60 g blue urethane beads
 139 g latex with 43.2 % solids
 45 g 2 % polyacrylic acid thickener
 0.5 g aqueous ammonia

After thorough mixing, the masses had viscosities of respectively 200, 150 and 260 poise. Coatings (0.1 mm thick wet) on untreated cotton fabric were prepared with each of these compositions. The coated fabric specimens were dried at approximately 65 °C, then heated to 150 °C for 30 min. Free film specimens were also manufactured, air-dried and then heated to 150 °C for 30 min. The following properties were observed:

Free film			Fabric coating	
Tensile strength kg/cm ²	100% modulus kg/cm ²	% elongation	WVT g/cm ² /h	Newark bending
28	8.4	610	6.5	No failure at 4,000,000
99	9.9	630	6	slight failure at 2,000,000
27.4	16.9	330	5	failed at 60,000

The coatings manufactured with 25 % and 50 % polyurethane beads were non-sparkling compared to those obtained with 10 % polyurethane beads. They had an appealing velvety, suede-like appearance.

Example XII

A covering dispersion was manufactured using the latex from Example IV with

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wood flour as filler. The wood flour had a particle size range of 20 to 100 µm. The following constituents were thoroughly mixed in a strong shearing mixer and then passed through a stone mill of 0.0127 cm distance, to obtain a mass with a viscosity of 210 poise:

30 g wood flour
 75 g mineral spirit
 20 g oleic acid
 10 g NH₃ (28-30 % NH₃)
 208 g latex with 43.2 % solids
 4 g sulfonated naphthalene-formaldehyde resin (Tamol SN)
 100 g 2 % aqueous polyacrylic acid thickener

Blade coatings were prepared on untreated cotton fabric and on free film, as in Example IX.

Free film			Fabric coating	
Tensile strength kg/cm ²	100 % modulus kg/cm ²	% elongation	WVT	Newark bending
19	19	140	9.4	fails at 74,000

This covering is receptive to traditional aqueous leather finishing agents, as was mentioned earlier for the preceding examples that use leather dust.

Example XIII

A covering dispersion was manufactured using the latex from Example IV and urea-formaldehyde beads with a particle size of 20-40 µm, in the following fractions:

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30 g urea-formaldehyde beads
 208 g latex with 43.2 % solids
 120 g 2 % aqueous polyacrylic acid thickener
 1 g concentrated aqueous ammonia

After mixing, the viscosity was 710 poise.

Free films and blade coverings were prepared on untreated cotton fabric as before.

Values for free film			Values for fabric covering	
Tensile strength kg/cm ²	100 % modulus kg/cm ²	% elongation	WVT	Newark bending
22	20	160	9.4	minor failure at 2,000,000

This covering had good wear resistance and was very receptive to traditional aqueous leather finishing agents.

Example XIV

Dispersions were manufactured from the latex of example IV and fine-particle, orange-pigmented polyvinyl chloride resin with particles in the size range of 10 to 150 μm .

- A) 30 g filler particles
208 g latex with 43.2 % solids
150 g 2 % aqueous polyacrylic acid thickener
1 g concentrated aqueous ammonia
- B) 60 g filler particles
139 g latex with 43.2 % solids
75 g 2 % aqueous polyacrylic acid thickener
1 g concentrated aqueous ammonia

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The viscosity was of 150 poise for the first and 75 poise for the second. Coverings and free film were prepared

Values for free film			Values for fabric covering	
Tensile strength, kg/cm ²	100 % modulus kg/cm ²	% elongation	WVT	Newark bending
A. 16	10	500	7	No failure at 4,000,000
B. 10.6	10	360	7.6	No failure at 4,000,000

The coverings had an appealing velvety appearance and very good wear resistance. They had an appropriate bending strength to be used for shoe uppers, or in upholstery.

Example XV

A polyether-polyurethane prepolymer was manufactured by reacting 9.76 mol polyoxypropylene triol with a mean molecular weight of 423, 52.8 mol polyoxypropylene diol with a mean molecular weight of 1,970 and 52.8 mol polyoxypropylene diol with a mean molecular weight of 1,016, with 243 mol toluene-di-isocyanate (80/20 mixture of 2,6-/2,4-isomers) for 4.5 h at 85 °C, to an isocyanate equivalent weight of 864. The prepolymer was then diluted with toluene to a solid content of 94 % and cooled to 50 °C, to be then reacted with 34 mol methyl-diethanolamine. This prepolymer was then emulsified in a high-speed mixer using the following formulation to obtain a cationic latex:

42.3 parts prepolymer

1.2 parts acetic acid
 56.5 parts deionized water

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A synthetic leather substrate was manufactured by dispersion of 308 g chrome-tanned leather fibers (Lorum Fiber Co. Y-020-015 fibers with 9 % water) in 11.35 L water with the aid of a small paper beater. It was then transferred to a 136 L box equipped with stirring and diluted with water to an overall slurry volume of 50.4 L at 15 °C. To this were added 1.7 g brown dye and 10.5 g sulfonated naphthalene-formaldehyde resin and mixed in. Then 2,090 g of the cationic polyurethane latex with 40.2 % solids from above were added, followed by 8.4 g $\text{Al}_2(\text{SO}_4)_3$, 42.0 g Na_2CO_3 and 420 g of a 1.2 % aqueous ammoniacal Karaya gum, to precipitate the latex. One fourth of this precipitated polymeride-leather slurry was transferred to a 50.8 x 50.8 cm manual sheet mold*; 35 g of 0.64 cm long 2 Denier nylon fibers predispersed in water were then added. The mass was then mixed to evenly disperse the leather fibers, nylon fibers and polymeride flock particles; liquid was then removed by drawing through a 30-mesh wire screen with 0.59 mm openings. The wet band so manufactured was removed, pressed between absorbent paper and dried for 30 min at 110 °C. The dried sheet was polished to ensure even thickness and exhibited the following properties:

WVT = 21 g/m²/h

Bally bending = very small surface cracks at 547,000 bend passes

This sheet provides a very desirable substrate for any of the coverings described above, to yield strong, tough leather substitutes.

An external covering dispersion was manufactured using the latex from Example IV and the orange-pigmented polyvinyl chloride particles from Example XIV as

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filler. The following constituents were used:

236 g latex with 42.5 % solids
 100 g orange-dyed polyvinyl chloride particles
 25 g 2% aqueous polyacrylic acid thickener
 1 g concentrated aqueous ammonia

To 200 g of the above mixture were added another 50 g of 2 % aqueous polyacrylic acid thickener, followed by centrifugation. The viscosity was 75 poise.

* "Handblattform" in the German original; no English equivalent found in any technical dictionary available [T.N.]

A 0.1 mm (wet) blade coating was prepared on the synthetic leather substrate described above, dried for 40 h at 65 °C and then melted for 30 min at 150 °C, then reconditioned at 21 °C and 50 % relative humidity. The water vapor permeability was 6 g/m²/h.

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Patent claims

1. Procedure for the application of a surface coating of a tough, flexible substrate sheet by covering this sheet with an aqueous dispersion that contains polyurethane and an organic, finely divided filler, and drying the covering obtained, **characterized by** the aqueous dispersion consisting of a polyurethane latex that consists of 10 to 70 wt.-% solids with 10 to 50 wt.-% of this solid in the form of the filler mentioned, consisting of particles with a mean diameter of 10 to 75 μm , where the aqueous dispersion has a viscosity of 30 to 2,500 poise and the polyurethane latex is manufactured from a reaction mixture that contains sufficient triol to create a crosslinking density in the range of 1 crosslinking per 10,000 to 7,500 hypothetical mean atomic weight units.
2. Procedure according to claim 1, **characterized by** the covering mentioned being polished, with an aqueous leather-finishing agent being applied to it.
3. Procedure according to claim 1, **characterized by** the filler being leather dust.
4. Procedure according to claim 1, **characterized by** the filler containing dyed elastomeric beads.
5. Procedure according to claim 1, **characterized by** the polyurethane comprising the reaction product of an organic poly-isocyanate and a polyoxy-alkene polyol, a free film of a latex of this polyurethane being formed with a tensile strength of 69 kg/cm², a fracture strain of 970 % and a modulus at 100 % elongation of 8.4 kg/cm².

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6. Procedure according to claim 1, **characterized by** the substrate sheet being split hide leather, fabric or a non-woven material.
7. Leather substitute material, manufactured according to the procedure of claim 1.